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Nancy D. Piltch
*National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio*

Jih-Fen Lei
*NYMA, Inc.
Engineering Services Division
Brook Park, Ohio*

and

Mary V. Zeller
*National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio*

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OXIDATION OF PALLADIUM-CHROMIUM ALLOYS FOR HIGH TEMPERATURE APPLICATIONS

Nancy D. Piltch
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Jih-Fen Lei
NYMA, Inc.
Engineering Services Division
Brook Park, Ohio 44142

and

Mary V. Zeller
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

An alloy consisting of palladium (Pd) with 13 wt % chromium (Cr) is a promising material for high temperature applications. High temperature performance is degraded by the oxidation of the material, which is more severe in the fine wires and thin films used for sensor applications than in the bulk. The present study was undertaken to improve our understanding of the physical and chemical changes occurring at these temperatures and to identify approaches to limit oxidation of the alloy. The alloy was studied in both ribbon and wire forms. Ribbon samples were chosen to examine the role of grain boundaries in the oxidation process because of the convenience of handling for the oxidation studies. Wire samples 25 μ m in diameter which are used in resistance strain gages were studied to correlate chemical properties with observed electrical, physical, and structural properties. Overcoating the material with a metallic Cr film did prevent the segregation of Pd to the surface; however, it did not eliminate the oxidation of the alloy.

INTRODUCTION

An alloy of Pd with 13 wt % Cr (henceforth referred to as PdCr) shows promise as a material for high temperature work, particularly for use in strain gages (refs. 1 to 3). The bulk material exhibits electrical stability up to 1000 °C, but the fine wires needed for strain gage applications oxidize at temperatures above 600 °C, with consequent degradation of the electrical conductivity. For higher temperature applications, a PdCr-based strain gage has to be coated with a mixture of alumina and zirconia (ref. 4) to prevent oxidation. The present study was undertaken to examine the oxidation mechanism of this alloy and the relative chemical and physical changes that occur at elevated temperatures. An alternative Cr coating was studied for its suitability as a protective coating. This study extended earlier experiments of Boyd et al. (ref. 5) on the same subject.

Samples of a PdCr alloy were studied in ribbon and wire forms because these geometries allow surface effects to be studied. Though the ultimate application at NASA Lewis will be with wires and thin films, the ribbons were studied extensively for convenience in handling and visualization and, more important, for examination of the role of grain boundaries in the oxidation process. The ribbons were 70 μm thick by 2.5 mm wide; the wires were 25 μm in diameter. The ribbon samples were a polycrystalline material produced in a spin-melt process resulting in irregular grains. The wire samples were obtained from four sources and were evaluated for suitability in high temperature strain gages.

EXPERIMENTAL METHOD

Ribbon samples were heated in air at temperatures of 600, 700, 800, 900, and 1000 $^{\circ}\text{C}$ for times ranging from 10 min to 2 hr. Not all times were represented at all temperatures. Wire samples were used as received and after heat treatment in air at 800 $^{\circ}\text{C}$ for 50 hr. After being cooled to room temperature, both ribbon and wire samples were studied by Auger electron spectroscopy (AES), Auger depth profiles, scanning electron microscopy (SEM), and energy dispersive x-ray (EDX) spectroscopy.

Auger scans were performed with a 5-kV electron beam and a magnification of 5000. The Auger depth profiles were performed by sputter etching with a 4-kV argon ion beam. The sputter rate was calibrated with a $\text{Ta}_2\text{O}_5/\text{Ta}$ standard and assumed to be the same for all species. A sputter rate of 12 nm/min was used throughout these studies. Recorded profiles were converted to approximate atomic percentages using the sensitivity tables incorporated in the spectrometer software. After profiling, both the sputter crater and unsputtered areas were examined by SEM and EDX. Two-dimensional maps of Pd and Cr distributions on the surface were obtained by EDX. The limited sensitivity of EDX to oxygen made it difficult to obtain useful maps of oxygen distribution. AES maps were attempted but did not have sufficient spatial resolution.

Additional ribbon samples were prepared for the oxidation protection study by sputter deposition of chromium on the surface to depths of 200, 50, or 20 nm. The coated ribbons were heated in air at 800 $^{\circ}\text{C}$ for 1, 5, and 20 hr. For the 200-nm samples, a thick, insulating oxide layer was formed on the surface. Because of the insulating nature of this surface, severe charging prevented the acquisition of surface AES scans, but AES depth profiles could still be obtained. The 50-nm samples were heated in air at 800 $^{\circ}\text{C}$ for intervals of 1, 5, 10, and 20 hr, and at 1000 $^{\circ}\text{C}$ for 5 hr. Additional samples were preheated at 800 $^{\circ}\text{C}$ for 1 or 5 hr and then heated at 900, 950, or 1000 $^{\circ}\text{C}$ for intervals up to 10 hr. Charging was not a problem for these samples with the thinner initial Cr layer.

Auger studies of the 25- μm -diameter wires were undertaken to correlate the chemical composition with observed electrical performance as well as with physical and structural properties as determined by EDX and SEM and by direct measurement of physical dimensions. All measurements were performed both on as-received wires and on wires that had been heat-treated at 800 $^{\circ}\text{C}$ for 50 hr. AES survey scans and depth profiles were obtained at several locations on each wire to obtain typical spectra despite the possibility of nonuniform composition throughout the wire. The very fine wires tended to heat up and move out of the analysis region when the electron beam impinged on them. To prevent this occurrence, the electron beam was defocused, the voltage reduced to 4 kV instead of the more usual 5 kV, and the beam current reduced to 10 nA or less instead of a few hundred nanoamperes, which is more typical with this instrument. This reduced the sensitivity to the point that trace contaminants could not be detected and spread the beam such that spatial resolution was degraded.

In a similar experiment to those performed on the ribbons, one PdCr wire was sputter-coated with 200-nm Cr by using a cylindrical sputter-deposition system. Both a bare wire and the Cr-coated wire were subjected to a 4-hr soak at 1000 $^{\circ}\text{C}$ and then to thermal cycling between 100 and 1000 $^{\circ}\text{C}$. The wire surfaces were then examined by SEM and EDX; no AES studies were performed on the coated wire.

RESULTS AND DISCUSSION

Figure 1 shows representative AES depth profiles for uncoated ribbon samples. The sample shown in figure 1(a) was heated to 800 °C for 60 min; that in 1(b) was heated to 1000 °C for 10 min. All samples heat-treated to 600, 700, and 800 °C had profiles similar to that in figure 1(a). All samples showed Pd segregation to the surface as seen in region A of the figure. Underneath this Pd layer was an oxide layer (shown in region B) consisting of Pd, Cr, and O. The depth to which this oxide layer persisted varied with the temperature and duration of heating. Region C shows a composition approaching that of the bulk alloy. At 900 °C, Pd enrichment was less pronounced, and at 1000 °C there was no distinctive Pd-rich layer, but rather an oxide region somewhat enhanced in Pd near the surface with no clear boundary between layers. The results for all temperatures are shown in table I.

The information from the AES profiles was supplemented by SEM photographs and EDX maps. Figure 2 shows typical SEM micrographs of ribbons heat-treated to 600, 700, 800, and 1000 °C. At 600 °C distinct grain boundaries were seen outlining polygonal grains that were approximately 5 to 10 μm across. At 700 °C the grain boundaries were decorated; EDX maps showed the grain boundaries to be enriched in Pd compared with the rest of the surface. At 800 °C the grain boundaries have lost this apparent decoration, but Pd is seen fairly uniformly distributed over the surface. At 900 °C (not shown) the morphology is beginning to change, with the grains becoming less well defined and islands of pure Pd starting to appear. By 1000 °C this islanding is seen over the entire surface.

The SEM and EDX results suggest that Pd is migrating to the surface through the grain boundaries. Since good maps of oxygen distribution were difficult to obtain, less evidence is available for the role of grain boundaries in oxygen transport. Oxygen is suspected to be diffusing inward at the grain boundaries, possibly through metallic Pd. Oxygen diffusion through the metal lattice or through the oxide scale may also be occurring simultaneously.

An attempt was made to correlate oxygen content (through oxide layer thickness) with the temperature and duration of heating. Scatter in the data prevented any meaningful kinetics results from being extracted. Such kinetics data were shown better by the thermogravimetric analysis (TGA) studies done by Boyd et al. (ref. 6), which presented oxidation rates for the PdCr alloy as a function of temperature.

The Cr-coated ribbon samples were then studied to test whether a dense Cr₂O₃ layer would be formed to seal the grain boundaries and prevent further diffusion of oxygen into the alloy. The first studies were of the samples coated with 200 nm of Cr and heat-treated as described in the Experimental Method section. No Pd was seen at the surface of these samples; instead, there was a layer of Cr₂O₃ whose depth was independent of heating time. Ribbon samples treated at 800 °C for 20 and 50 hr showed the same oxide layer thickness. This suggested that the Cr coating did protect the underlying alloy as desired.

The charging problems referred to in the Experimental Method section made the acquisition of surface AES spectra difficult for the samples with a 200-nm Cr coating. The next studies were with a much thinner initial Cr thickness of 50 nm. These samples were heat-treated in air at either 800 or 1000 °C. At 800 °C the oxide formed at the surface as it had in the earlier samples. This layer did not increase in thickness after 1 hr of heat treatment. Additional samples with a 20-nm coating showed similar properties.

After heating in air for 1 hr at 1000 °C, the profile was similar; that is, there was an oxide layer at the surface above the bulk and no Pd-enriched region. However, the thickness of the oxide layer was greater than that at 800 °C, implying that the protection was incomplete and that Cr was being abstracted from the alloy and oxidized. The thermogravimetric studies of Boyd et al. (ref. 6) showed that the rate of oxygen diffusion through chromium oxides increases above 800 °C. Figure 3 shows a profile of a ribbon with 20 nm of Cr heat-treated at 800 °C for 15 hr and at 900 °C for 1 hr. This profile is very different from those of the uncoated ribbons shown in figure 1.

For the wire samples, the intent was to identify chemical differences leading to differences in electrical properties. SEM micrographs (shown in fig. 4), were recorded along the length of the as-received wires. These micrographs show that wire sample 4 had a distinctly different surface structure from the other three wires.

In the AES depth profiles of the as-received wires, samples 1 and 2 showed the least amount of oxygen in the bulk, below the detection limits of the instrument (about 1 to 2 at %). Wire sample 4 showed oxygen persisting well into the bulk at depths greater than 600 nm. The bulk composition of all wires showed that samples 1 and 2 had the highest Cr content, matching the nominal 13 wt % of the intended alloy whereas the others were below that value. EDX composition showed some Si and Al contamination of all wires below the detection limits of AES. Numerical values are not shown since the accuracy of the measurements is limited by the sensitivity of the instrument under the operating conditions needed for the experiment. In addition, the large electron beam spot size (after defocusing) relative to the size of the wires and the size of the sputter crater on the rounded surface made it impossible to identify the depth to any meaningful extent; values determined from the profiles were actually averages over large segments of the wires.

Figure 5 shows SEM micrographs in cross section for the wires that had been heat-treated in air at 800 °C for 50 hr. All wires show an outer layer surrounding the wire (shown by EDX to be Pd that had segregated to the surface) and an oxide layer just beneath this. This oxidation behavior is similar to that seen in the ribbon samples. Wire samples 1 and 2 were the most uniform both in cross section and along the length and also had the thinnest oxide layer.

EDX images of the heat-treated wires showed islands of Pd similar to those seen in the ribbons. Palladium enrichment was seen at the surface in the AES scans. Samples 1 and 2 showed the largest amount of surface-segregated Pd. Sample 4 showed the largest oxygen content at all depths from the surface and into the bulk. Sample 3 also was oxidized to a greater extent than 1 and 2. All wires showed some variability in composition along their lengths. The composition results showed that those wires with the greatest Pd surface enrichment, thinnest oxide layer, largest Cr concentration in the bulk, and smallest O concentration in the bulk were the same wires that exhibited the best electrical performance. The AES studies were not able to show differences between samples 1 and 2, although SEM micrographs and electrical performance were somewhat different for them. Since the AES measurements are limited in spatial extent, they will not be sensitive to differences resulting from localized variations in physical or chemical structure which may influence electrical properties. Again, because of sensitivity limitations, numerical values of composition are not indicated here, but trends are indicated below for samples 1 to 4:

Surface Pd enrichment:	2 ~ 1 > 3 ~ 4
Surface O concentration:	4 > 3 > 1 > 2
Bulk Cr concentration:	2 ~ 1 > 3 ~ 4
Bulk O concentration:	4 > 3 > 1 ~ 2

For the Cr-coated wire, figure 6 shows that the Cr coating did change the time dependence of the electrical resistance. The resistance of the coated wire at 1000 °C increased with time, in contrast to bare wires for which the resistance decreased with time. Although the total change in resistance of the coated wire was less than that of a bare wire, the drift rate of a bare wire decreased with time whereas the drift rate of the coated wire remained approximately constant even after a 4-hr soak at 1000 °C. This result indicates that the Cr coating decreased the oxidation rate of the wire, although it was not sufficient to protect the wire completely from further oxidation.

Figure 7 shows that coating the wire with Cr changed both the slope and linearity of the resistance-versus-the-temperature curve $(R - R_0)/R_0$. This curve of the coated wire was less linear and exhibited large hysteresis. For these reasons, the Cr coating was unsuitable to strain gage applications and has not been used.

CONCLUSIONS

The Auger electron spectroscopy (AES) and energy dispersive x-ray spectroscopy (EDX) data for the ribbon samples showed evidence of the migration of Pd through the grain boundaries. At temperatures of about 700 °C, the grain boundaries showed Pd enrichment; by 800 °C the Pd spread over the entire surface. Islanding of Pd was seen at some locations on the surface at 900 °C and was widespread over the entire surface at 1000 °C. The mechanism for oxidation was not determined by these experiments. Attempts to quantify the oxygen transport into the bulk were discontinued because of the data scatter.

Coating the ribbons with Cr prior to heat treatment caused a layer of Cr₂O₃ to form on the surface. This oxide layer did inhibit further oxidation at 800 °C but did not prevent oxidation of the bulk alloy at temperatures above 800 °C. In all cases the Cr overlayer prevented the segregation of Pd to the surface, but for samples heated to 1000 °C, the thickness of the oxide layer continued to increase with time. This Cr overcoat did not passivate the surface at temperatures above 800 °C.

The AES scans of the wires were consistent with the electrical, physical, and structural properties measured by other techniques. The wires with the highest Cr concentration, least oxygen concentration in the bulk, and most uniform composition are also those with the best electrical behavior. The limited sensitivity of the Auger spectrometer for these very small wires prevented detection of trace species, so their possible effect on electrical properties remains undetermined. This limited sensitivity and large sampling region compared with the size of the wires also made quantitative measurements of composition less reliable.

As a result of these studies, wire sample 2 was selected for continued strain gage applications. This selection was determined by electrical measurements showing the least change in electrical resistance with temperature. This selection was further supported by chemical studies of the composition, by SEM and EDX results showing the thinnest and most uniform oxide layer, and by physical measurements showing the least change in wire diameter after heat treatment.

The results for the Cr-coated wires suggest that Cr overcoating does inhibit oxidation of the wires, but the degradation of the electrical performance made this technique unsuitable for strain gage applications.

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TABLE I.— APPROXIMATE THICKNESSES OF Pd-RICH AND OXIDE LAYERS OF HEAT-TREATED Pd RIBBON SAMPLES

[Thickness determined by Auger depth profiles.]

Temperature, °C	Duration, min	Thickness of layer, nm	
		Pd ^a	Oxide ^b
600	30	100	320
600	60	110	400
600	90	170	830
700	30	220	880
700	90	580	780
700	120	520	850
800	10	140	500
↓	20	180	980
↓	30	170	770
↓	60	120	820
↓	90	150	960
900	10	130	700
900	20	50	350
900	30	70	330
1000	10	(a)	^b 310
↓	20	↓	^b 420
↓	30	↓	^b 670
↓	60	↓	^b 560

^aNo attempt was made to determine the Pd layer separately for the 1000°C samples.

^bThe oxide layer thickness is the thickness from the surface to the bulk for the 1000°C samples.

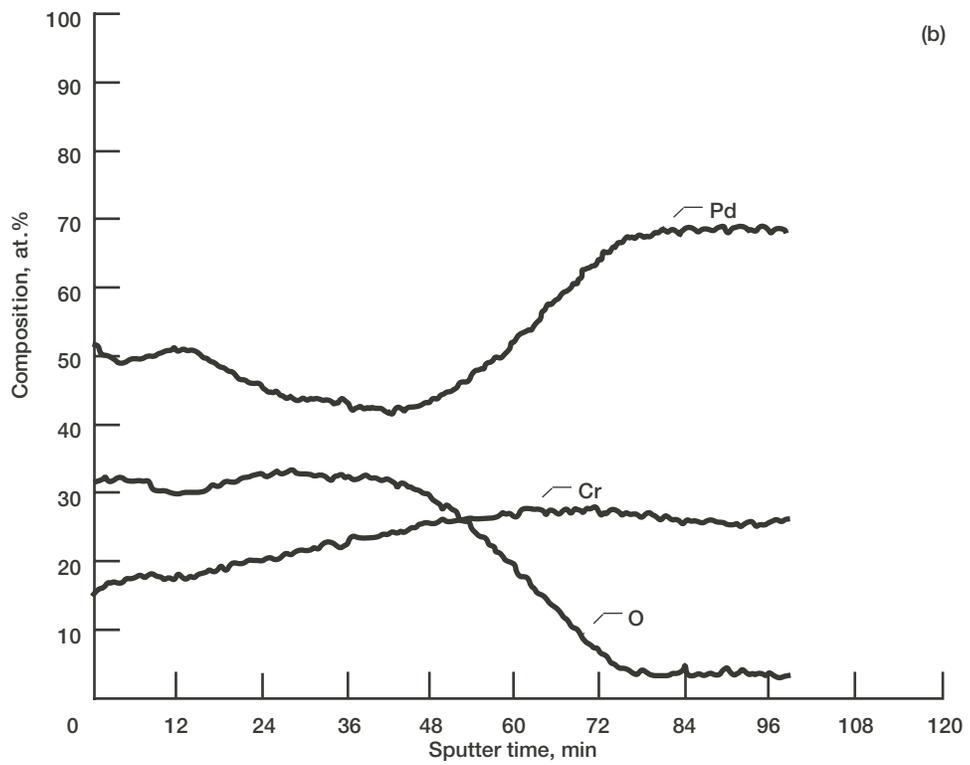
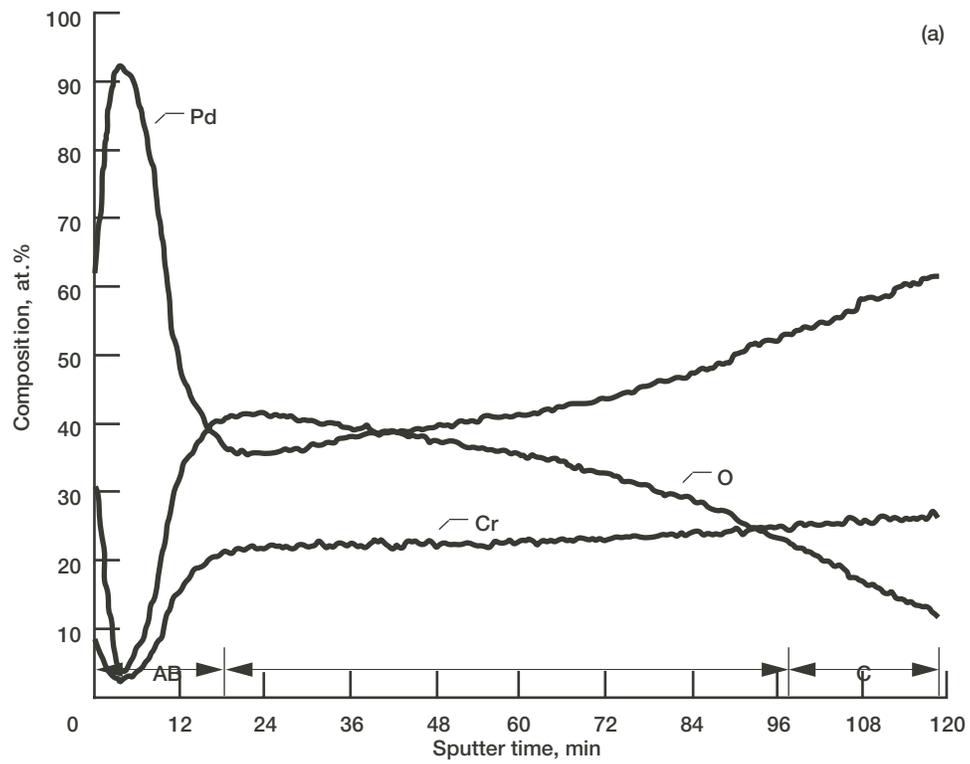


Figure 1.—Auger electron spectroscopy (AES) profiles of uncoated heat-treated PdCr ribbon samples. Sputter rate, 12 nm/min. (a) 800 °C for 60 min. (b) 1000 °C for 10 min.

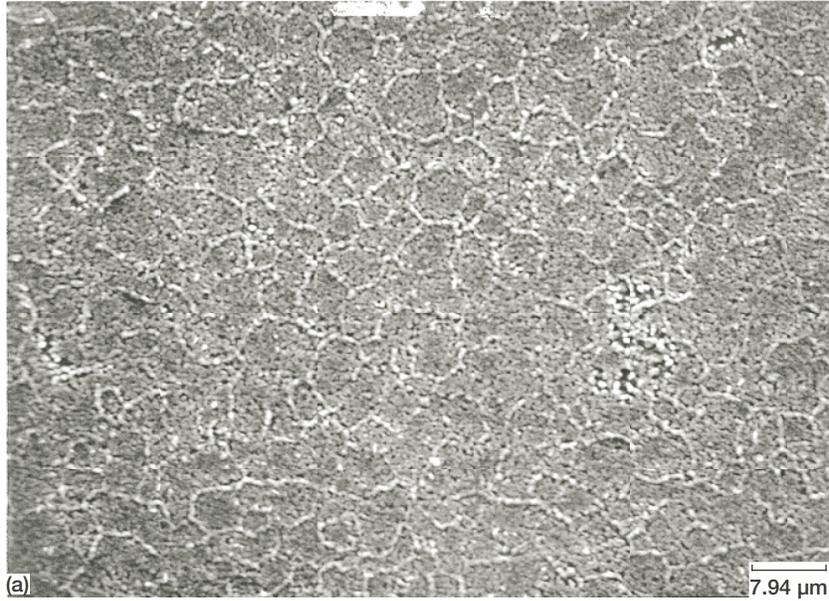


Figure 2.—Scanning electron microscopy (SEM) micrographs of heat-treated PdCr ribbon samples. (a) 600 °C for 60 min. (b) 700 °C for 60 min. (c) 800 °C for 20 min. (d) 1000 °C for 10 min.

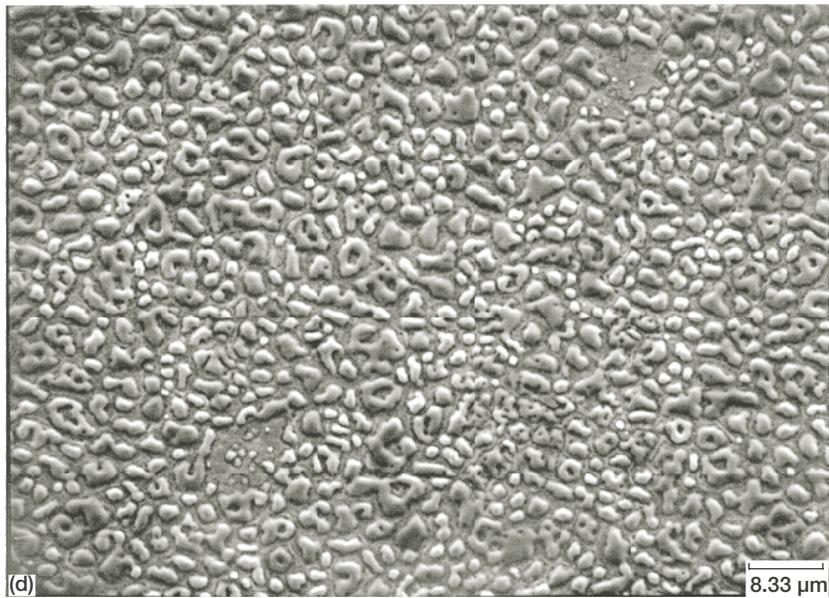
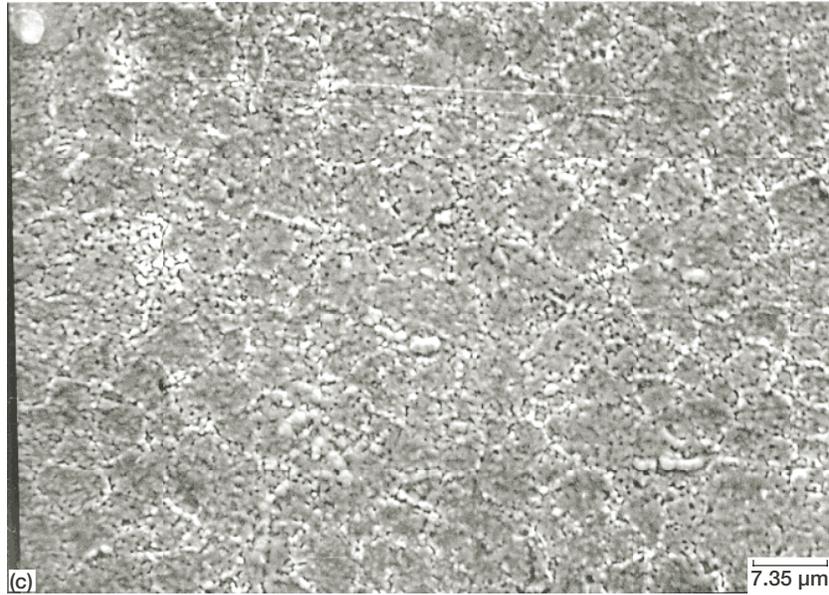


Figure 2.—Concluded. (c) 800 °C for 20 min. (d) 1000 °C for 10 min.

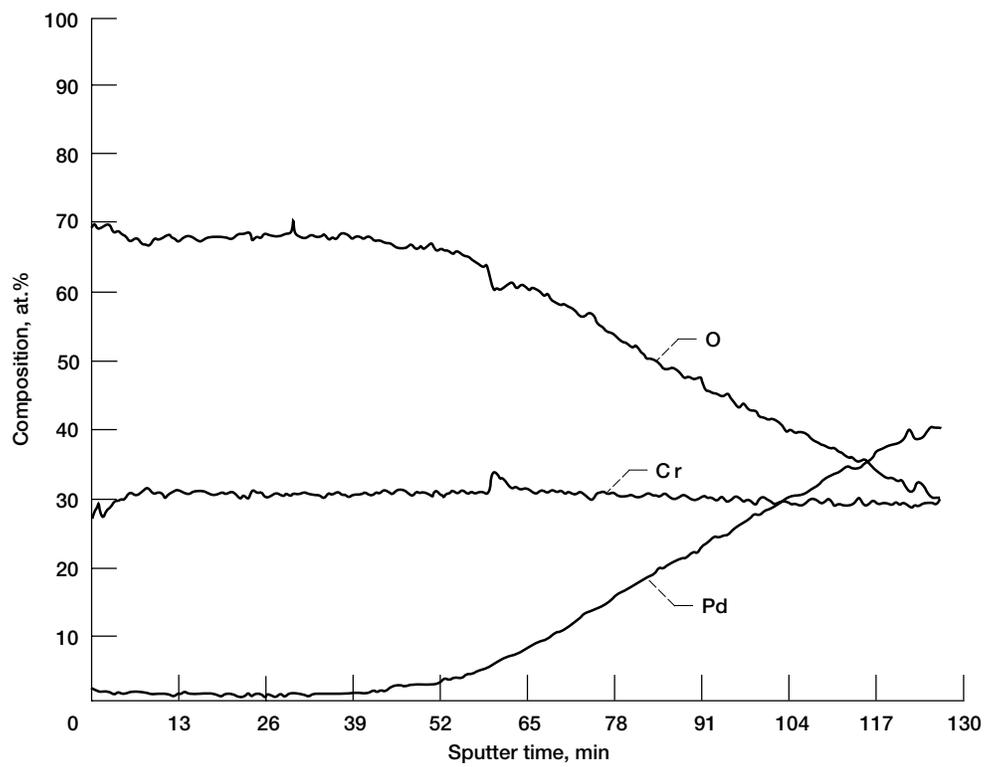


Figure 3.—AES profile of PdCr ribbon with 20-nm Cr overcoat. Heat treated at 800 °C for 15 hr followed by 900 °C for 1 hr. Sputter rate, 2.5 nm/min.

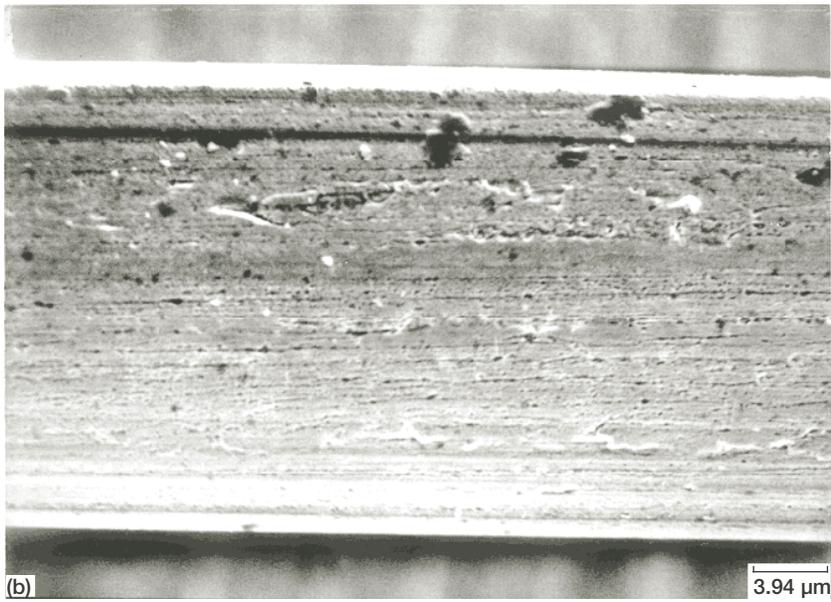


Figure 4.—SEM micrographs of as-received PdCr wires. (a) Sample 1. (b) Sample 2. (c) Sample 3. (d) Sample 4.

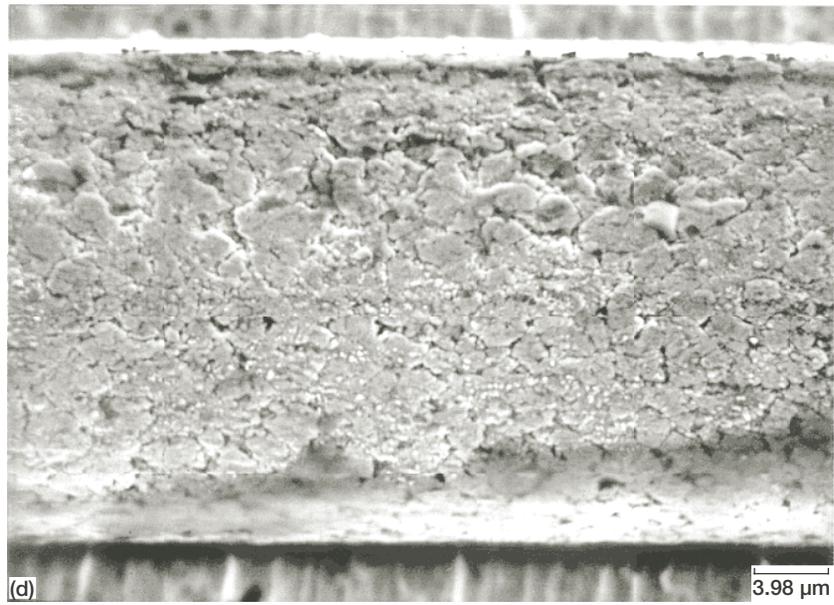
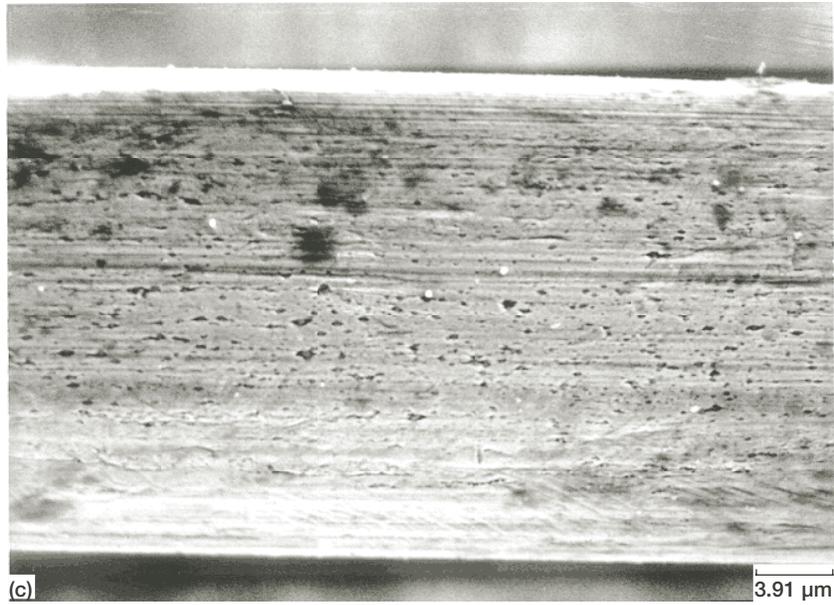


Figure 4.—Concluded. (c) Sample 3. (d) Sample 4.

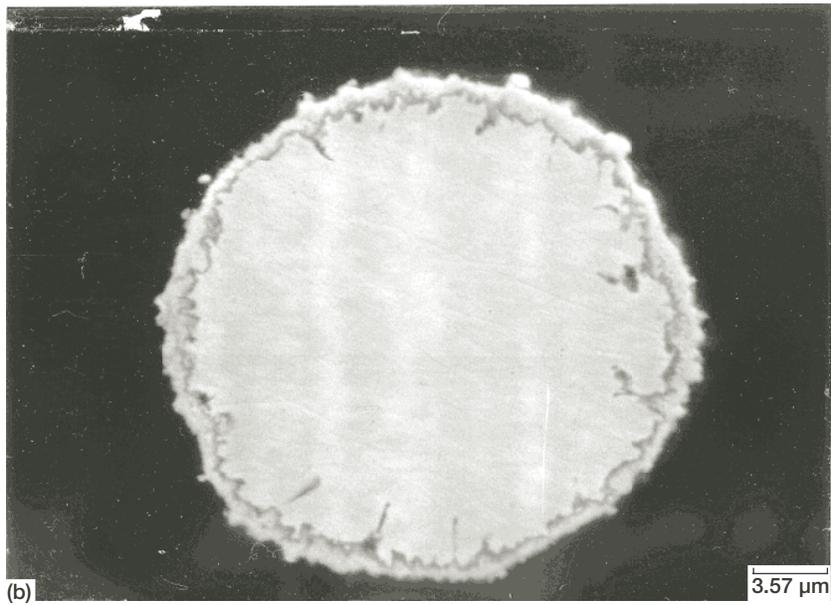
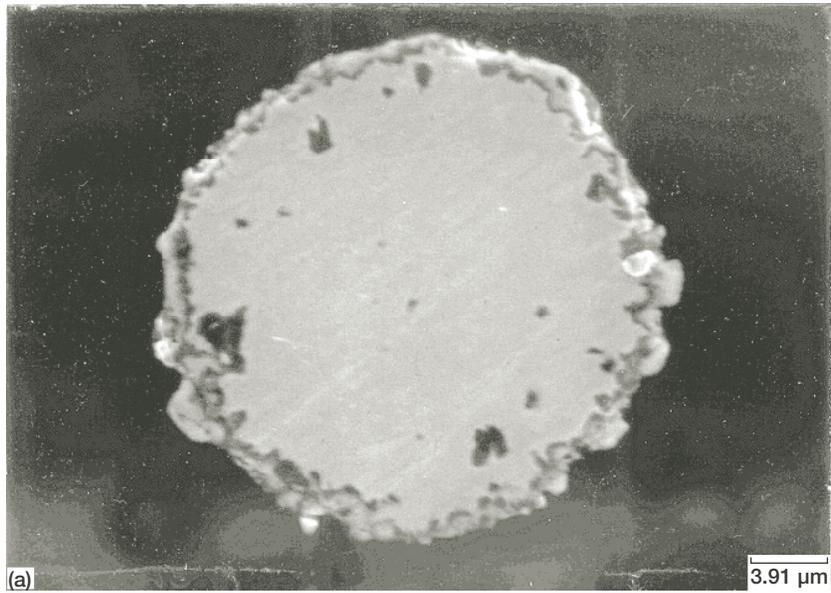


Figure 5.—SEM micrographs of PdCr wire cross sections heat treated at 800 °C for 50 hr. (a) Sample 1. (b) Sample 2. (c) Sample 3. (d) Sample 4.

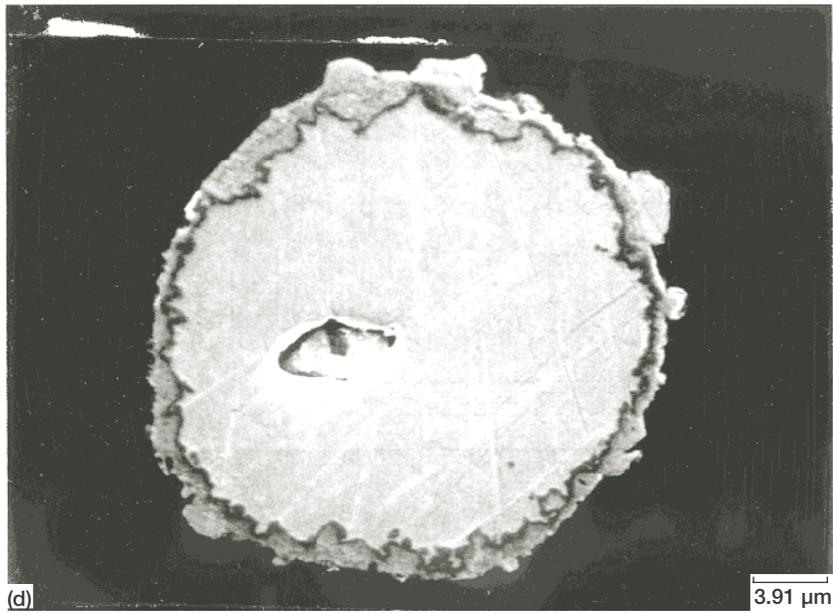
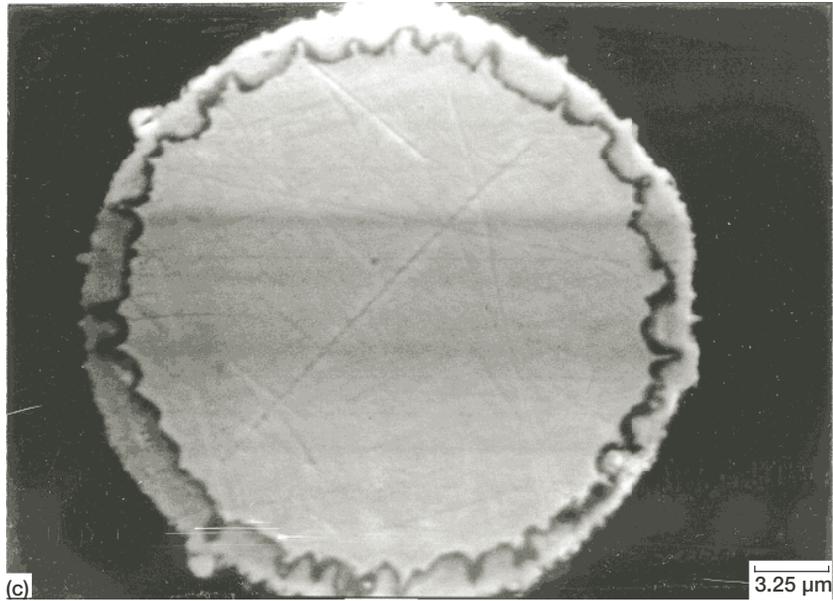


Figure 5.—Concluded. (c) Sample 3. (d) Sample 4.

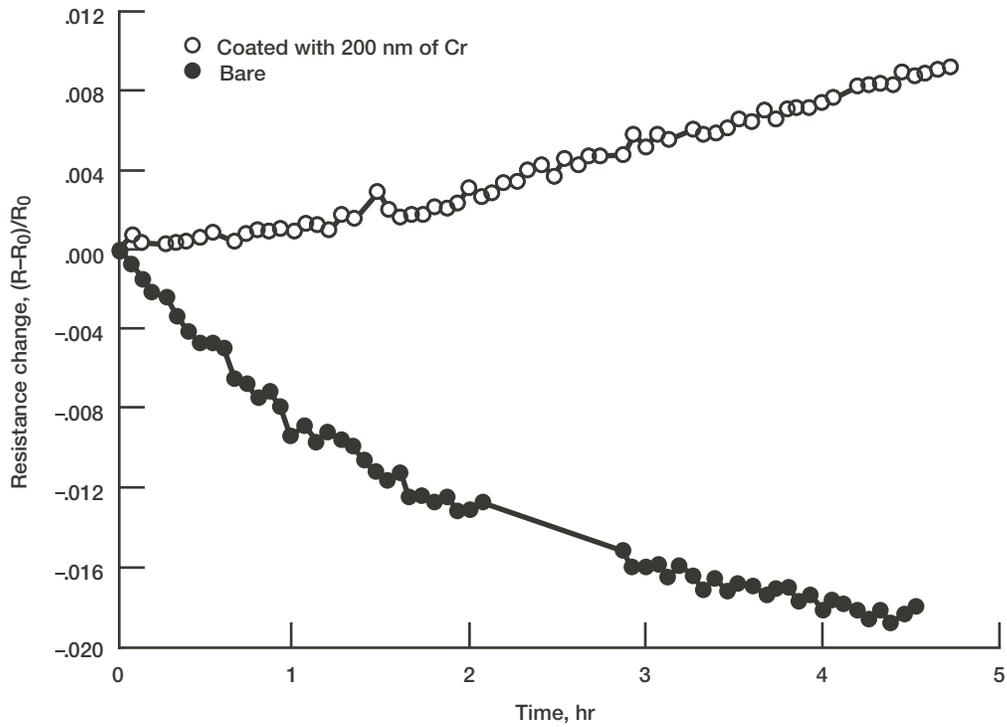


Figure 6.—Resistance drift during 4-hr soak at 1000 °C for bare and uncoated PdCr wires.

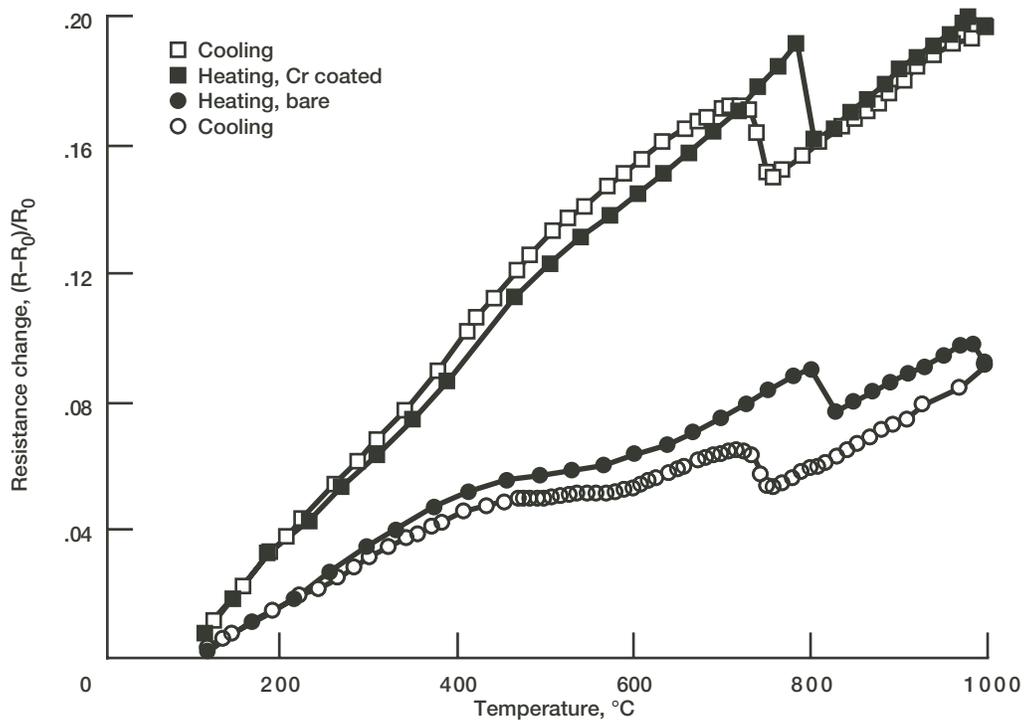


Figure 7.—Resistance versus temperature of bare and Cr-coated PdCr wires tested after 4-hr soak at 1000 °C.

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